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# Electrical study on Carboxymethyl Cellulose-Polyvinyl alcohol based bio-polymer blend electrolytes

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**Abstract**. The present work deals with the formulation of bio-materials namely carboxymethyl cellulose (CMC) and polyvinyl alcohol (PVA) for bio-polymer blend electrolytes (BBEs) system which was successfully carried out with different ratio of polymer blend. The biopolymer blend was prepared via economical & classical technique that is solution casting technique and was characterized by using impedance spectroscopy (EIS). The ionic conductivity was achieved to optimum value 9.12 x $10^{-6}$ S/cm at room temperature for sample containing ratio 80:20 of CMC:PVA. The highest conducting sample was found to obey the Arrhenius behaviour with a function of temperature. The electrical properties were analyzed using complex permittivity $\varepsilon^*$ and complex electrical modulus $M^*$ for BBEs system and it shows the non-Debye characteristics where no single relaxation time has observed.

## 1. Introduction

Bio-polymer blend electrolytes (BBEs) have drawn great attention due to their prospective applications in electrochemical devices for instance rechargeable batteries, fuel cells, super capacitors, and solar cells [1-2]. Various types of polymers from natural and synthetic sources have been studied extensively to pursue the development of BBEs system. Among the natural polymer, chitosan [3], carrageenan [4], polyactides [5], and carboxymethyl cellulose [6] are favorable in the preparation of polymer electrolytes. Whereas from synthetic sources, polyethylene oxide (PEO) [7], polyvinyledene fluoride (PVdF) [8], polyacrylonitrile (PAN) and polyvinyl alcohol (PVA) [9] are also suitable polymers as they offer relatively higher conductivity. Carboxymethyl cellulose is a cellulose derivative from the regenerated cellulose $[C_6H_{10}O_5]n$ with backbone consist of D-glucose residues linked by β-1,4-linkage [10]. CMC polymer binder is certain to provide multipoint interaction in building stable solid biopolymers (SBEs). Owing to its characteristic, CMC is widely used as filming, emulsification, suspension, water maintaining, bind and inspissation [11]. Another potential candidate is the polyvinyl alcohol (PVA) which is claimed to give advantage in the application of composite films due to its hydrophilicity properties. PVA has the structure where its carbon chain backbone has attached hydroxyl group (-OH) to methane carbon, making it to be the source of intermolecular attraction forces which is significant to form bio-polymer blends electrolytes (BBEs) [12].

Blending is a technique that involves mixing of two or more different polymers without the formation of covalent bonding [13]. The ionic conductivity of the polymer blend can be enhanced compared to

single polymer [14]. The blending study has been focusing on intermolecular interaction in governing the ionic conductivity [15]. The incorporation of CMC into carrageenan as reported by Rudzhiah [16] has proved that blending can increase the ionic conductivity via the formation of H-bonding. On top of that, CMC has ability to form hydrogen bonds due to the existence of characteristic functional group carboxylate anion ($-COO^-$) and hydroxyl (–OH). Therefore, it is expected for the BBEs of CMC and PVA to be the platform with tailored individual properties in numerous applications. The blending method is believed to improve the ionic conductivity properties by changing the structural behavior [17].

Ionic conductivity is the most crucial property of polymer electrolyte, thus, researchers have shown an increasing interest to discover the interactions between the two polymers and to achieve the desired performance in different applications. A study on the dielectric properties of CMC [18] and PVA [19-20] has been reported previously. In the case of CMC, the electric structure is unipolar thus having similar dielectric properties like other polyelectrolytes. PVA is well known to have chain flexibility attributed to the intra- or inter-molecular attraction which is focusing at the hydroxyl (-OH) group. The advantage offered by PVA can accommodate the segmental motion and rotation to the relaxation process during formation of H-bonding between the two polymers.

Most of the BBEs system offers low ionic conductivity at room temperature. Knowledge about electrical properties of the polymer electrolyte is beneficial in order to study the interaction during blending which is expected to happen in this present work. The present work is an attempt to study the electrical properties carboxymethyl cellulose (CMC)-polyvinyl alcohol (PVA) as the bio-polymer blends electrolytes (BBEs) which were prepared by using solution casting method at various ratio compositions. The BBEs system was analyzed via the electrical impedance spectroscopy (EIS) for the evaluation of electrolyte composition that exhibits the highest electrical conductivity at ambient temperature. The increase in chain flexibility of the CMC/PVA based BBEs is the key factor for the enhancement of the ionic conductivity.

## 2. Materials and methods

### *2.1. Preparation of sample*

Polymers studied in the present work were procured from Acros Organic Co. for CMC and Merck Co. for the PVA. The molecular weight of CMC and PVA of approximately 90000 and 70000 were used in this work. In the preparation of BBEs solution, total weighed amounts of granules PVA and powder CMC, 2.0 g was dissolved directly in distilled water. The dissolution was done at temperature 55 °C under constant stirring. The CMC/PVA solutions were prepared at different weight percentage 100/0, 90/10/ 80/20, 70/30, 60/40, 50/50 and 40/60 (%/%). The notation of sample compositions is tabulated in Table 1. These solutions were casting into glass petri dishes and put in the oven for about 5 hours at 60 °C. The process was accompanied by further drying in the desiccator to ensure all solvent has been evaporated.

**Table 1.** List of designation of CMC/PVA with their composition respectively.

| Sample Designation | CMC/PVA blends (%) |
|---|---|
| C1 | 100/0 |
| C2 | 90/10 |
| C3 | 80/20 |
| C4 | 70/30 |
| C5 | 60/40 |
| C6 | 50/50 |
| C7 | 40/60 |

### *2.2. Characterization*

*2.2.1. Impedance analysis*. The dielectric properties of the bio-polymer blend CMC/PVA electrolyte film with different ratios were tested by using HIOKI 3532-50 LCR Hi-Tester over the frequency range from 50 Hz to 1 MHz at room temperature. The BBEs sample was cut into small disks with are of 2 cm diameter and sandwiched between two stainless steel electrodes of the sample holder. The bulk resistance ($R_b$) value was obtained from the plot of imaginary impedance ($Z_i$) versus real impedance ($Z_r$) and the ionic conductivity, σ was determined using equation (1) below:

$$\sigma = \frac{t}{R_b A} \tag{1}$$

where t is a thickness of the sample and A ($cm^2$) the cross-sectional area of the BBEs film. The thickness of the bio-polymer electrolytes was found to be in the range of 0.0093 to 0.0914 cm using a digital thickness gauge (DML3032)

*2.2.2. Complex permittivity (ε*).* Complex permittivity is important to explain the mechanism and interactions of ions in the BBEs system [15]. The complex permittivity can be defined as:

$$\varepsilon^* = \varepsilon_r + j\varepsilon_i \tag{2}$$

where $\varepsilon_r$ is the dielectric constant (real part of complex permittivity) and $\varepsilon_i$ is the dielectric loss (imaginary of complex permittivity), can be calculated using equation as follows:

$$\varepsilon_r = \frac{Z_i}{\omega C_o (Z_r^2 + Z_i^2)} \tag{3}$$

$$\varepsilon_i = \frac{Z_r}{\omega C_o (Z_r^2 + Z_i^2)} \tag{4}$$

*2.2.3. Complex modulus(M*).* The complex modulus is needed to highlight the suppression of electrode polarization and bulk dielectric behaviour of the BBEs system. The real modulus, $M_r$ and imaginary modulus, $M_i$ was calculated using the following equation:

$$M_r = \frac{\varepsilon_r}{(\varepsilon_r^2 + \varepsilon_i^2)} \tag{5}$$

$$M_i = \frac{\varepsilon_i}{(\varepsilon_r^2 + \varepsilon_i^2)} \tag{6}$$

## 3. Results and discussion

*3.1. Impedance studies*

Figure 1 depicts the Cole-Cole plot of CMC/PVA based BBEs films at room temperature. The Cole-Cole plot of BBEs containing 0, 10, 20, 30 and 40 percent composition of PVA showed by Fig 1(a-e) shows an incomplete semicircle curve. Two regions could be observed as semicircle at high frequency and spike at low frequency. These impedance plots are frequently used to separate the electrical polarization that affects the selected impedance frequency and the impedance of bulk material as reported earlier [21].

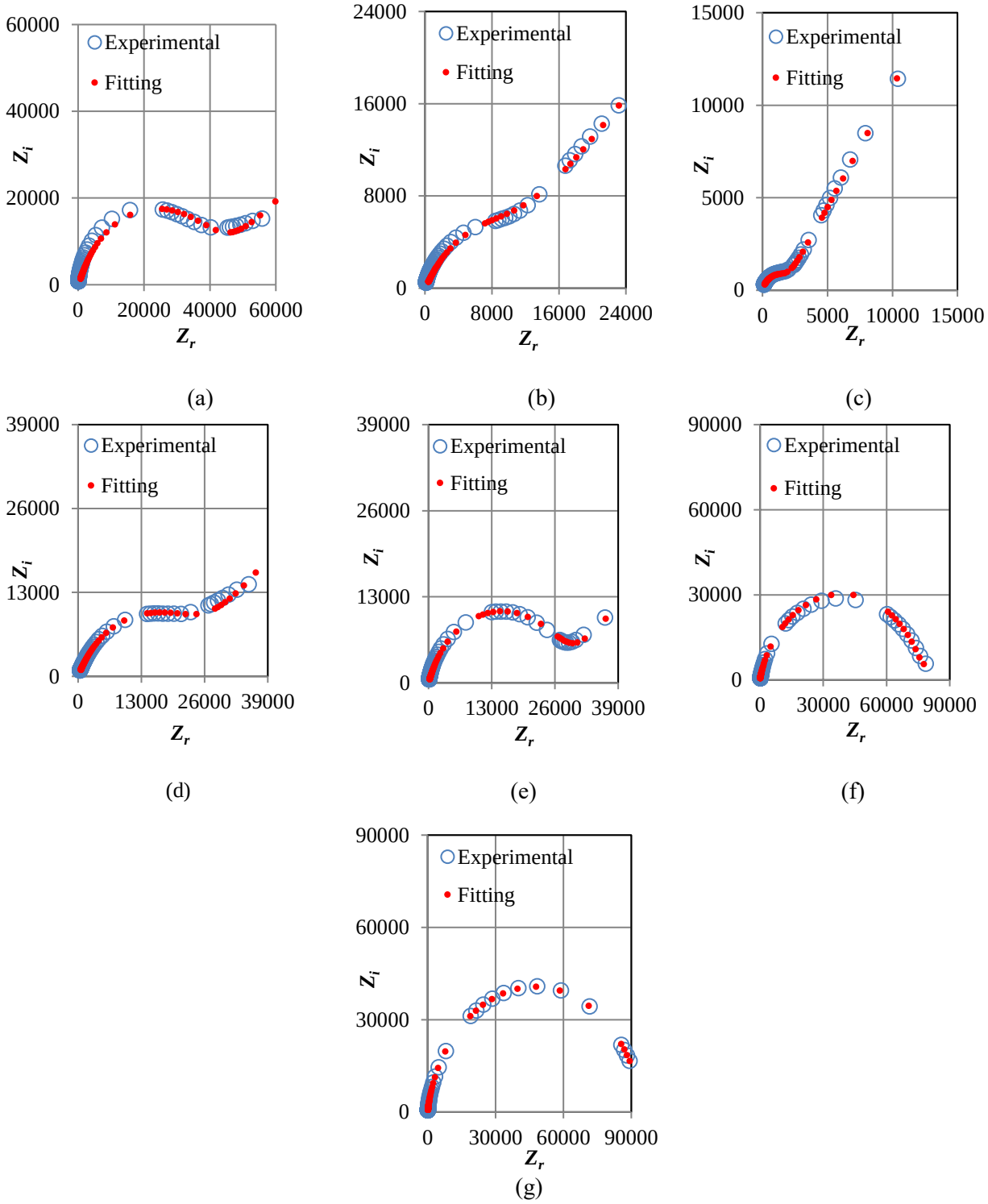



**Figure 1**. Cole-Cole plot of CMC/PVA based bio-polymer blend electrolytes system for composition (a) 100:0 (b) 90:10 (c) 80:20 (d) 70:30 (e) 60-40 (f) 50:50 (g) 40:60.

In this work, the impedance data for the shows semicircle and spike that can be represented by a parallel combination of bulk resistance ($R_b$) and constant phase element (CPE). The $R_b$ was determined

based on the interception between higher and lower frequency from the Cole-Cole plot of complex impedance [22-23]. CPE was utilized in a model to replace the capacitor to balance the heterogeneity of the BBEs system studied in this work. The impedance of CPE ($Z_{CPE}$) can be represented by the following equation:

$$Z_{CPE} = 1/k(j\omega)^p \text{ where } 0 \leq p \leq 1 \quad (7)$$

Or

$$Z_{CPE} = k\,[\cos(p\pi/2) - j\,\sin(p\pi/2)]\,/\omega^p \quad (8)$$

Variable of $k^{-1}$ corresponds to the capacitance value of the CPE element, ω is the angular frequency where, $\omega = 2\pi f$ (f is frequency), and $p$ is referred to the deviation of the vertical axis in the $Z_r$ versus $Z_i$ plot. The values of $Z_r$ and $Z_i$ associated to the equivalent circuit can be termed as follows:

$$Z_r = \frac{R_b + R_b^2 k_1^{-1} \omega^{P_1} \cos(\frac{\pi p_1}{2})}{1 + 2R_b k_1^{-1} \omega^p \cos\left(\frac{\pi p_1}{2}\right) + R_b^2 k_1^{-2} \omega^{2p_1}} + \frac{\cos \pi p_2/2)}{k_2^{-1} \omega p_2} \quad (9)$$

$$Z_i = \frac{R_b^2 k_1^{-1} \omega^{P_1} \sin(\frac{\pi p_1}{2})}{1 + 2R_b k_1^{-1} \omega p_1 \cos\left(\frac{\pi p_1}{2}\right) + R_b^2 k_1^{-2} \omega^{2p_1}} + \frac{\sin \pi p_2/2)}{k_2^{-1} \omega p_2} \quad (10)$$

Table 2 lists the parameter of the circuit elements for all BBEs composition studied at room temperature. The formation of semicircle could be explained by the occurrence of a capacitor and a resistor, which is in parallel series. Meanwhile, an inclined spike was due to the effect of electrode polarization, which is the characteristic of ions diffusion process for the bio-polymer blends electrolyte system [24]. This diffusion happens among ions when PVA was incorporated into CMC and causes the insulating properties start to change into semi-conducting material. As shown in Figure 1 (c-f), when PVA was incorporated into the CMC the tilted spike has inclined at an angle lesser than 90° along the real axis which might be attributed to heterogeneity between the electrode-biopolymer electrolyte interface and resulting to a decrease in ionic conductivity [25]. These result support previous research conducted by [26], which has explained on the electrical properties of CMC, doped with $NH_4Br$.

Figure 1 (f) and (g) shows the only semicircle curve after the addition of more than 50 percent composition of PVA into the BBEs system. This is directly related to the bulk resistance and bulk capacitance of the BBEs system [27]. The part of semicircle shown in the Cole-Cole plot can be demonstrated as a parallel resistor attributed to the movable ions inside the polymer matrix and capacitor due to the motionless polymer chain circuit network. The addition of more PVA in C5 until C7 will destruct the dielectric polarization and lead to greater hindrance to the polymer resulting in an increase in $R_b$ and decreasing the ionic conductivity.

**Table 2.** List of parameters of circuit elements for all BBEs system composition at room temperature.

| ***Sample*** | ***$p_1$* (rad)** | **$C_1$(F)** | ***$p_2$* (rad)** | **$C_2$ (F)** |
|---|---|---|---|---|
| **C1** | 0.850 | $5.5 \times 10^8$ | 0.430 | $5.58 \times 10^5$ |
| **C2** | 0.775 | $4.56 \times 10^8$ | 0.495 | $9.90 \times 10^5$ |
| **C3** | 0.745 | $5.82 \times 10^7$ | 0.585 | $1.44 \times 10^6$ |
| **C4** | 0.749 | $9.60 \times 10^7$ | 0.499 | $8.35 \times 10^5$ |
| **C5** | 0.810 | $1.40 \times 10^8$ | 0.472 | $2.05 \times 10^5$ |
| **C6** | 0.839 | $2.60 \times 10^8$ | - | - |
| **C7** | 0.901 | $8.85 \times 10^8$ | - | - |

### *3.2. Conductivity studies*

There were numerous efforts adopted for the development of the bio-polymer blend electrolytes in order to enhance the ionic conductivity. CMC is the most potent candidates as host polymer due to low cost, eco-friendly and can offer better chemical and physical properties [22, 25]. Despites the advantages, CMC has limitation as the conductance property is relatively low. Thus, one of the alternatives to increase the conductivity of CMC is the incorporation of high dielectric permittivity dipolar polymer such as PVA. As shown in Figure 2, the ionic conductivity of CMC/PVA based BBEs has increased until the composition 80:20 which suggests the optimum amount of PVA. The electron donating group, carboxylate anion of CMC backbone mainly coordinates with the PVA and produces the ion-dipolar complexes via intra- or inter-chain hopping between the functional group the two polymers during the blending process. This interaction in such blend matrix was able to increase the flexibility of polymer chain via process of forming or breaking the ion-dipolar bonds that exist between the CMC/PVA which served as the host polymer. Consequently, the conductivity of the CMC/PVA can achieve the optimum value, which is 9.12 x $10^{-6}$ S/cm due to higher flexibility of polymer chain that can fasten the segmental dynamic of the BBEs system studied in this present work.

The result obtained similar to chitosan/PVA based bio-polymer blend electrolyte conducted by Buraidah [12] which managed to obtain conductivity of 1.77 x $10^{-6}$ S/cm. For sample containing more than 20% of PVA the optimum concentration has exceeded because at this concentration, ion association is more significant than ion dissociation and disables the interaction between CMC and PVA [28]. This will decrease the number of mobile ions within the bulk of the BBEs and therefore decreasing the conductivity. The plot of log conductivity versus reciprocal temperature is shown in figure 3. The correlation between conductivity and temperature for the highest conducting sample, C3 obeys the Arrhenius law with the regression value, $R^2$ approaching to 1 indicating the BBEs system was thermally assisted [29].

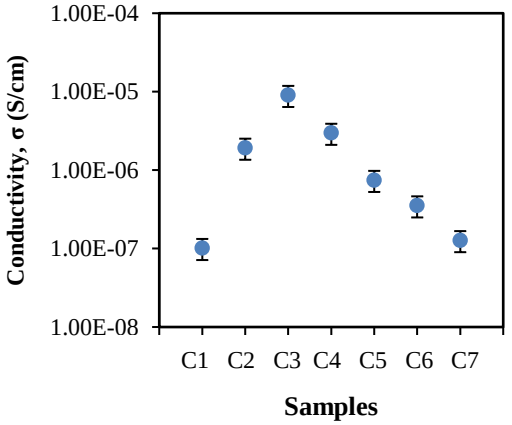



**Figure 2.** The ionic conductivity of CMC/PVA BBEs system at room temperature.

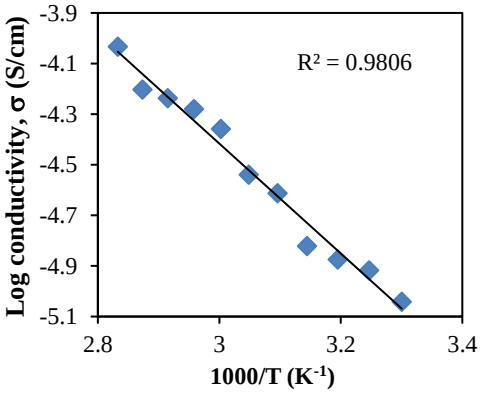



**Figure 3.** Temperature dependence for the highest conductivity CMC/PVA (80:20 compositions).

### *3.3. Electrical studies*

The dielectric properties may vary in different types of polymer electrolyte system attributed to several factors including frequency of applied electrical field, temperature, structural characteristics or other external factors. Figure 4 (a) and (b) shows the frequency dependence of the real part of the dielectric constant ($\varepsilon_r$) for all composition of CMC/PVA bio-polymer blend electrolytes system which is also known as stored charge in any material. In the studied range of frequency of 50Hz to 1 MHz, it can be observed $\varepsilon_r$ and $\varepsilon_i$ increases sharply from low frequency contributed by electrode, molecular and ionic

polarization. The dielectric constant, $\varepsilon_r$ was found to increase for the sample C3 which indicated that charge carrier concentration has increased in the space charge accumulation area and later increasing the conductivity [30]. Sample C3 shows the highest value of $\varepsilon_r$ may be due to an increase in the heterogeneity in the polymer blend which could increase the free volume. At high frequency, both dielectric properties were showed decreasing trend explained the decreasing rearrangement of dipolar groups and polar segments of the polymer which is no longer capable to react to the applied electric field hence causes electrical relaxation process to happen [31].

Modulus formalism is important to analyze the ionic conductivity or in further analysis as the loss peak could not be detected in the dielectric loss spectrum. It is a useful application to analyze the electrical response and relaxation of polymer electrolyte system. The real ($M_r$) and imaginary ($M_i$) part of complex modulus are derived from their complex permittivity and shown in figure 5. In figure 5 (a), the $M_r$ values were increased proportionally with the increase of frequency. According to Ramesh [32], the non-zero values of $M_r$ at low frequency suggest that the BBEs system was negligible from electrode polarization. Plot of imaginary modulus ($M_i$) able to evaluate the effect of the smallest capacitance and the largest resistance, hence determine the relaxation process attributed to short or long-range movement of charge carrier as reported by Sinclair and West [33]. The occurrences of relaxation peaks in the $M_i$ plots in figure 5(b) reveals the characteristic of the BBEs system as ionic conductors [29]. The peak position and height of C1 sample at high frequency can be distinguished from other samples in both $M_i$ and $M_r$ spectrum may be due to the bulk effect as CMC is exceptionally stiff which in turn resulting to a decrease in chain mobility. This peaking curve also attributed to the relaxation phenomenon in the polymer electrolyte system.

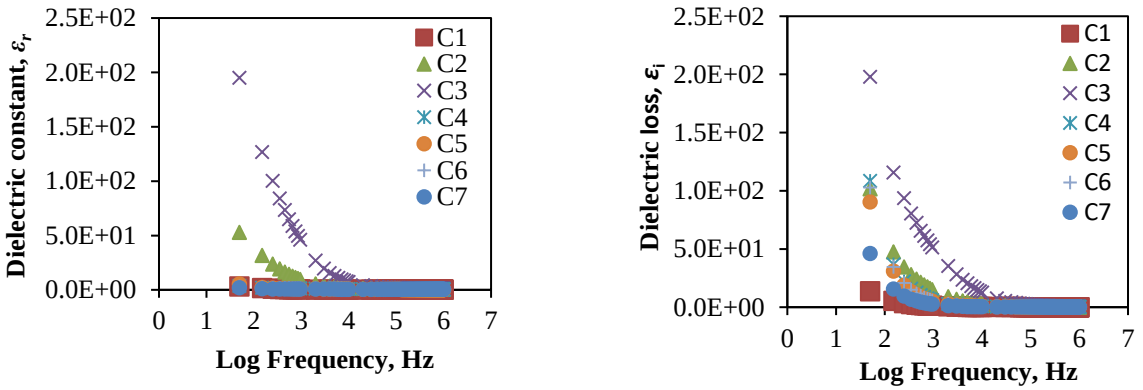
Compared with CMC, the CMC/PVA based BBEs contribute much more to the $M_r$ of the blend, which becomes broadening and lowering down which means that stiffness of CMC has decreased as PVA was added [34]. At lower frequency, there was a large association between the values of capacitance with electrodes which can be seen by a plateau peak for $M_r$ and this present work result was in agreement with work done by Samsudin [28]. Thus, this confirmed that the behaviour of BBEs system work in this study is non-Debye.

Figure 6 illustrates the variation of real modulus ($M_r$) and imaginary modulus ($M_i$) parts of electrical modulus for the highest conductivity sample containing 80:20 compositions of CMC/PVA. Both figure 6(a) and (b) show long tails at lower frequency indicating that no relaxation peaks at that region. Figure 6(a) shows an increasing trend at higher frequency with no definitive peaks. In addition, the highest peak frequency of the highest conducting BBEs sample, C3, presented in Figure 6(b) which was corresponding to the shortest relaxation time [29]. Accordingly, the relaxation time decreases as temperature increases. At higher temperature the ion mobility of the polymer chain has increased and hence increasing the conductivity. This result also supports the work done by Pradhan [35].

Dielectric loss tangent (tan δ) spectrum of CMC/PVA in Figure 7 depicts the dielectric relaxation process which is derived from the ratio $\varepsilon_i/\varepsilon_r$. Sample C1 until C5 exhibits a relaxation peak at high frequency corresponding to the conductivity relaxation process, whereas sample C6 and C7 decreased sharply from lower to higher frequency. The dielectric and conductivity relaxation was evaluated by the reorientation process of dipolar molecules in the polymer which is represented by a peak in the tangent dielectric loss spectrum. The highest conducting sample, S3 exhibits the shortest relaxation time at higher frequency due to the increasing number of segmental motion [36]. Meanwhile slower relaxation process was indicated by higher PVA composition more than 50 percent composition which gives reflection to a lower conductivity. Figure 8 presented the plot of tan δ versus log frequency. The trend was clearly observed where tan δ shifts to higher frequency and the height of the peak also increased when temperature increased. Based on the plot of tan δ, the relaxation time, τ can be determined by using the following equation:

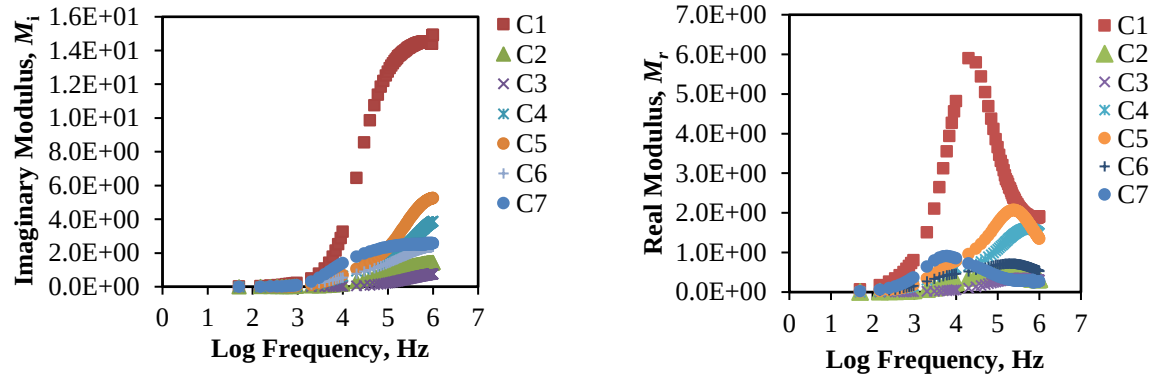
$$\tau = 1/\omega_{peak} \tag{11}$$

where $\omega_{peak}$ is the angular frequency of the relaxations peak. The temperature dependence of relaxation time for C3 BBEs is shown by figure 9 with regression value ($R^2$) of 0.9764. The plot shows good linearity and confirms the conductivity of temperature dependence of the present work BBEs system follows the Arrhenius law. The effect of temperature also suggests that there was no phase transition in the BBEs containing 80:20 composition of CMC/PVA and this result was in line with previous study on bio-polymer blend electrolytes of starch and methylcellulose [37].




(a) (b)

**Figure 4.** Frequency dependence of (a) dielectric constant (b) dielectric loss for various composition of CMC/PVA at room temperature, 303 K.




(a) (b)

**Figure 5.** Frequency dependence of (a) real modulus (b) imaginary modulus for various composition of CMC/PVA at room temperature, 303 K.

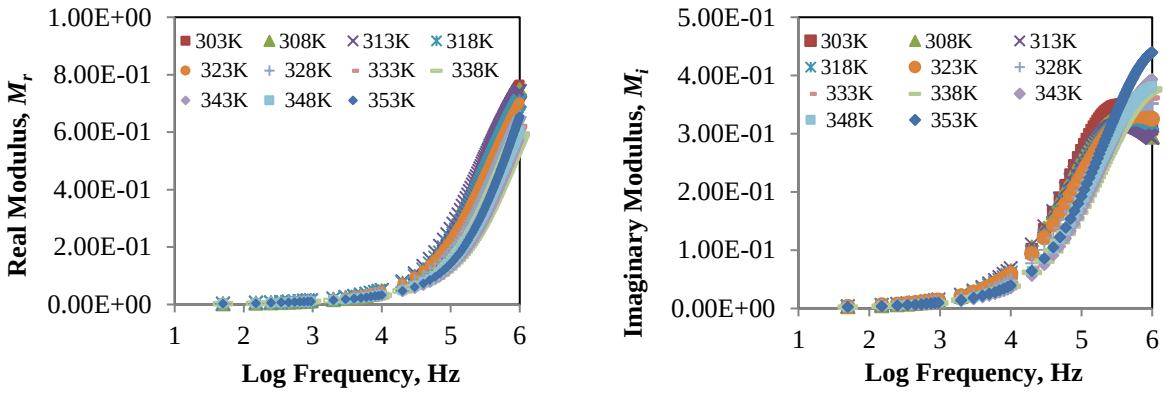



**Figure 6**. Frequency dependence of (a) real modulus (b) imaginary modulus for the highest conductivity CMC/PVA (80:20 compositions) at different temperature.

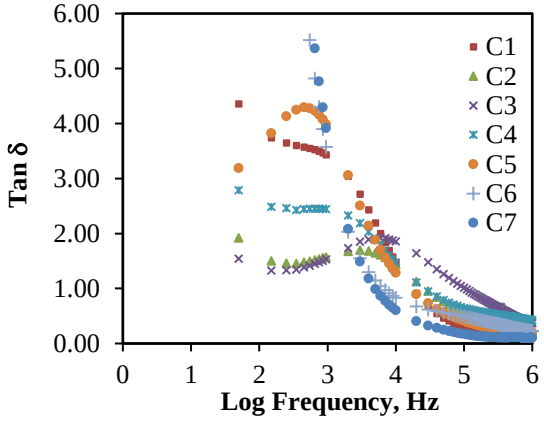



**Figure 7.** The dependence of tan δ on frequency for all compositions of CMC/PVA.

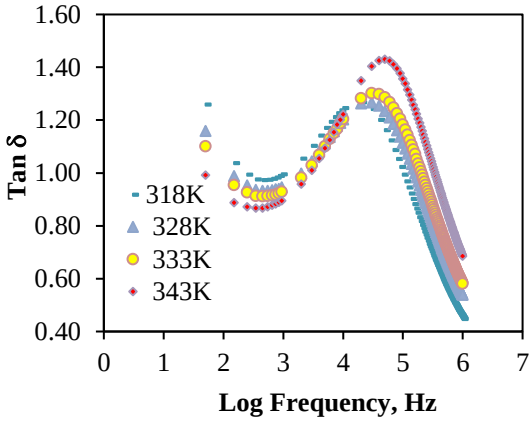



**Figure 8.** The dependence of tan δ on frequency of the highest conductivity CMC/PVA (80:20 compositions) at different temperature.

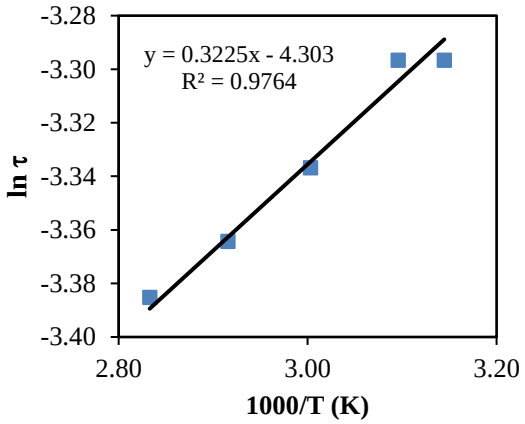



**Figure 9.** The temperature dependence of relaxation time of highest conductivity CMC/PVA (80:20 compositions).

## 4. Conclusion

The study of complex permittivity $\varepsilon^*$ and complex electrical modulus $M^*$ for BBEs system is a powerful approach to investigate the characteristic of molecular and ionic interaction towards the enhancement of ionic conductivity. The bio-polymer blend electrolytes containing CMC and PVA in a ratio of 80:20 prepared via casting solution method shows the highest ionic conductivity among all the test samples at ambient room temperature which is $9.12 \times 10^{-6}$ S/cm. The dielectric constant and dielectric loss decrease with increasing frequency that is explained by the accumulation of ions contributed by electrode, molecular and ionic polarization. The occurrence of peak in the imaginary modulus ($M_i$) confirmed the BBEs system is non-Debye characteristic. According to temperature dependence study of the highest conductivity, CMC/PVA system is thermally activated and follows the Arrhenian characteristics where $R^2$~1. Based on the result obtained, the conductivity of CMC/PVA based BBEs is still relatively lower compared to the reported conductivity of polymer electrolytes as this is the preliminary study. Thus, the conductivity of CMC/PVA can be enhanced with the addition of salt and/or plasticizer.

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